

● THE REVERSIBLE PROCESS IN THERMODYNAMICS

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HERE IS presented here a criticism of certain errors that appear quite commonly in textbooks on thermodynamics. It is not claimed that all textbooks have been examined or that no other errors exist. Within the means available the best that can be offered is a sample of the literature, a sample sufficiently biased toward the more authoritative writers to establish this point: that it would be well if students of thermodynamics were presented with a concept of the reversible process that does not contradict the fundamental notions of mechanics.

The textbooks of 15 authors have been examined and only two of these, Trevor's (1927) and Duhem's (1902), have avoided errors in defining the reversible process. Trevor's statement is perhaps too austere for students, but Duhem's is a model of clarity that could have been used to advantage by the many writers who followed him.

THE REVERSIBLE PROCESS

The reversible process is a concept fundamental in the development of thermodynamic theorems. Its exact definition is therefore a matter of importance. An examination of certain texts, representing writers of high reputation, has revealed, however, an apparent reluctance to define the reversible process with proper precision; the preference seems to lie in the direction of describing the properties of the reversible process and in presenting what are claimed to be examples. Since the concept is a limiting case which both actual and theoretical processes can approach but never attain, this manner of treatment causes confusion in the minds of students alert enough to recognize the contradiction, and it certainly has the disadvantage of only indirectly hinting at a concept that can be stated simply and directly as the limiting value of a mathematical function. There is hardly any doubt that the writers on thermodynamics recognize clearly the mathematical nature of the concept. Their failure to define it precisely is probably the result of trying to write down to the level of supposedly unprepared minds.

The favorite approach to the concept is through a consideration of the expansion of an ideal gas in a cylinder provided with a weightless, frictionless piston. If the pressure outside the piston is zero, so that the gas expands against a vacuum, no work will be done during the expansion; and since no energy will be expended, the temperature of the gas will not change. If a finite pressure, P , exists outside the piston, work will be done during each increment of expansion:

$$\Delta W = P \Delta V$$

Here ΔW is the work done during a change in volume ΔV of the enclosed gas. The total work done at the end of the process, when the pressure inside the cylinder equals the outside pressure will be

$$W = \int_{v_1}^{v_2} P dV \quad (1)$$

Here the gas has expended energy; consequently its temperature will decrease. If, however, the expanding gas be heated at such a rate that its temperature remains constant during expansion, the pressure within the cylinder will decrease more slowly and the gas will be able to expand farther before its pressure is equal to the outside pressure. It will therefore be able to perform a greater amount of work against the outside pressure. The expression (1) still holds but in this case v_2 has been increased. This type of expansion, called isothermal, is of particular interest. Since the temperature of the gas has not changed during expansion, its internal energy is likewise unchanged, and the energy expended in performing work is derived solely from the thermal energy supplied to hold the temperature constant. It now remains to be seen whether, during a given expansion of the gas from v_1 to v_2 , a still greater quantity of thermal energy can be converted into work. The expression (1) shows that this can be done by increasing the outside pressure P on the piston. Means must be provided, however, for keeping P always less than p , the pressure inside the cylinder, during expansion from v_1 to v_2 , for if P is initially nearly equal to p , very little expansion will take place unless P is continuously decreased.

It is therefore clear that the amount of thermal energy convertible into work for a given isothermal expansion will increase as the difference $p - P = e$ decreases. It is also clear that negative values of e need not be considered as in that case compression instead of expansion would occur. Further, if $e = 0$, the gas will be in equilibrium with the outside pressure and expansion will not occur. For all cases in which expansion occurs, therefore, e must have finite positive values. But as e decreases, the work performed, W , increases and our object is to determine the limit of W as e approaches zero.

From the gas law, we write

$$pv = RT$$

where R is the molar gas constant and T is the absolute temperature. In the isothermal expansion we are considering, RT is a constant, and we find that

$$pdv + vdp = 0$$

and

$$dv = -\frac{RT}{p^2} dp$$

Substituting this value of dv in (1) we have

$$W = -RT \int_{p_1}^{p_2} \frac{P}{p^2} dp$$

Using the relation $p = P + e$,

$$W = -RT \int_{p_1}^{p_2} \frac{P}{p(P+e)} dp$$

and

$$\begin{aligned} \lim_{e \rightarrow 0} W &= -RT \int_{p_1}^{p_2} \frac{dp}{p} \\ &= RT \log \frac{p_1}{p_2} = RT \log \frac{v_2}{v_1} \end{aligned} \quad (2)$$

It should be emphasized that the limit approached by W is not a value of W and therefore does not represent the work performed in any expansion however small e is chosen, so long as e remains finite and positive.

Similar reasoning may be used to study the changes in other forms of energy, such as the production of electrical energy through chemical reactions. It will be found that in all cases the amount of energy converted increases as the difference between the driving force and the opposing force decreases. The amount of energy converted from one form to another, therefore, approaches a limit increasingly as e approaches zero.

Only two authors have been found, among those studied in preparing this paper, who present precise definitions of the reversible process that do not contradict more fundamental concepts. Trevor's book (1) contains this definition:

Reversible Path. A continuous one-dimensional set of states of thermodynamic equilibrium, connecting two arbitrary states a and b of a given body, is not a path of the change of state ab . But the set may be the limit approached by the paths of a family of paths of the change ab , and also of the reversed change of state ba , when these changes of state are conducted with extreme slowness under the influence of the independently controlled forces and temperatures. When the prescribed set is such a limit it is termed a prescribed *reversible path* of the change of state ab , and of the reversed change of state ba . And the limits of the quantities of work and heat absorbed on the paths of the change ab , which are equal to the negatives of the work and heat absorbed on the paths of the change ba , as the limiting path is approached, are termed the work and heat absorbed on the *reversible path* ab , or developed on the reversible path ba .

The reader will readily identify "the limits of the quantities of work and heat absorbed on the paths of the change ab " with the limit of the work performed given by expression (2).

Pierre Duhem's definition (2) also lacks nothing in clarity.

THE FALLACY OF DISCONTINUOUS CHANGE

Trevor and Duhem furnish the only known exceptions to the common mistake of writers to associate the limit given by expression (2) with a hypothetical process car-

ried out so as to yield the limiting value of work done and heat absorbed. The term "reversible process" itself unfortunately suggests a process that is attainable, at least theoretically. Our next task is to show that a reversible process is not attainable, even theoretically, without introducing notions that contradict fundamental concepts of mechanics.

It has been shown that the limiting value of the work done in the isothermal expansion of a gas must be computed by letting $p - P = e = 0$: that is, by assuming the opposing pressure equal to the driving pressure. Under these conditions, of course, the gas will be in equilibrium with its surroundings and no expansion will occur. Writers nevertheless postulate expansion under equilibrium conditions and thereby contradict the fundamental notion of equilibrium. They are, in general, aware of this difficulty and employ various expedients to extricate themselves. Glasstone (3) for example says:

Since a reversible change must be performed at an infinitesimally slow rate, it follows that at any instant the system as a whole is virtually in temperature and pressure equilibrium with its surroundings; for this reason, a reversible process has been defined as a succession of equilibrium states.

Now it is clear that any change that occurs by passing through a series of equilibrium states implies discontinuity of change, so that the system either passes from one equilibrium state to the next in no time at all, or else if time does elapse, the system is nonexistent during the interim. This is probably the first time discontinuous change has been seriously considered since the famous attempts to deal with Zeno's paradox. However, this is not peculiar to Glasstone; he is only following the lead of a long line of predecessors.

Getman (4) describes a reversible cycle, which is merely a series of reversible processes, as:

... one which is carried out by applying infinitesimal changes under conditions such that the system is at all times practically in a state of equilibrium.

Roberts (5) says of the reversible process: "Throughout the process the gas is in equilibrium with its surroundings."

Guggenheim (6) says the reversible processes are a limiting case between "natural" processes (those that occur in nature) and "unnatural" processes (those that do not occur in nature) and asserts that "... they consist of a passage of a system in either direction through a continuous series of states of equilibrium."

MacDougall (7) used similar phrases in the 1926 edition of his text but abandoned them in the 1939 edition.

Partington (8) states: "A reversible change is a continuous succession of equilibrium states; it is an *ideal* change."

Epstein (9) writes:

It is possible to follow through by thermodynamical methods only processes which take place so slowly that they can be regarded as a succession of states of equilibrium. Strictly speaking, the change of the system in a finite time must be even infinitesimal and the rate of change infinitely slow.

Such infinitely slow processes have an important theoretical advantage in that they are *reversible*—that is, they can be gone through in both directions.

Lewis and Randall (10) put it this way:

Let us imagine a process so conducted that at every stage an infinitesimal change in external conditions would cause a reversal in the direction of the process; or, in other words, that every step is characterized by a state of balance. Evidently a system which has undergone such a process can be restored to its original state without more than infinitesimal changes in external systems. It is in this sense that such an imaginary process is called reversible.

CONFUSION OF THE LIMIT WITH A VALUE OF THE FUNCTION

In all of these excerpts it is apparent that the writers recognize the concept of the reversible process as the limit given in expression (2), but commit the error of identifying it with a value of the function. As we have seen, this has led to the necessity of postulating discontinuous change through a succession of equilibrium states.

The five-volume "Treatise on Physical Chemistry" by Taylor and Glasstone (11) now in publication is probably the most comprehensive effort of its kind ever attempted in this country. The section on thermodynamics treats the reversible process in terms similar to those used in Taylor's earlier work of the same title and avoids mention of discontinuous change during equilibrium. The only source of confusion is contained in the following statements:

The value [of the work done in isothermal expansion] attains a maximum when the driving pressure of the gas is infinitesimally greater than the opposing pressure. . . . The maximum external work is therefore done when driving and opposing forces differ infinitesimally.

Getman (4) also says:

The total work becomes larger and larger as ΔV is made smaller, and it attains a maximum value in the limiting case where ΔV approaches zero.

Hinshelwood (13) concludes:

In general, any change is said to take place reversibly when the driving force exceeds the opposing force by an infinitesimally small amount. A reversible change is the nearest possible approach to the limiting case where driving and opposing forces are equal, that is, to a state of equilibrium.

And finally, quoting Butler (14):

The maximum work is obtained . . . when the opposing forces, against which the work is done, are only infinitesimally less than the forces which tend to make the process go forward.

Here we need only observe that the function expressing the work done is such that no "maximum" or "nearest possible approach" exists; the work done approaches its limiting value asymptotically. Stated otherwise, no matter how small e , the difference between the driving and opposing forces, is chosen, there exists a smaller difference for which the work done is greater.

THE ERROR OF TEMPORAL REVERSIBILITY

In the expansion of a gas, there seems to be no way to regard the process as other than the result of a decrease

in the outside pressure. Some writers, however, would have the term "reversible process" imply a reversibility in time, thus introducing a new formal contradiction. For example, Partington (8) says:

A process which can be performed backwards so that all changes occurring in any part of the direct process are *exactly* reversed in the corresponding part of the reverse process, and no other changes are left in external bodies, is called a *reversible process* in the thermodynamic sense.

Roberts (5) states:

The reason why such a change is called reversible is that, if the process is carried out in the reverse direction, the whole system goes through exactly the same series of changes in the reverse direction.

Taylor and Glasstone (11) write: "In the ideal [reversible] process, all of the stages of the process may be repeated in inverse order in point of time. . . ."

This idea may have been suggested by earlier writers for in 1869 Briot (15) expressed the same idea.

If we regard the expansion of a gas as the result of a decrease in outside pressure and thus confer temporal precedence on the decrease in outside pressure, it is clear that the reverse process in point of time would require that the gas undergo compression before the outside pressure is increased. Of course, these writers did not intend that such an absurdity be inferred from their statements. Again it appears that the difficulty stems from trying to identify the value of the limit with a value of the function.

THE PROBLEM OF THE THERMOSTAT

In deriving the expression for the work done in isothermal expansion, it was postulated that the temperature remain constant without attempting to show how this might be accomplished even theoretically. Since the discussion was purely mathematical, the temperature was regarded as a parameter to be held constant for the purpose of differentiating with respect to pressure and volume. Thus any consideration of theoretical means of attaining isothermicity would have been extraneous. Certain authors, for example Hinshelwood, MacDougall (1939), Roberts, and Butler, assume a constant temperature without any reference to theoretical means of attaining it.

But these authors are exceptional. In most textbooks, where an expansion is said to be theoretically attainable in the limiting case, we find the author feeling obliged to describe a method of securing isothermicity. Usually he immerses the cylinder of expanding gas in a sufficiently large thermostat and carries out the expansion so slowly that, in the words of Glasstone, ". . . the absorption of heat keeps pace with its expenditure and the temperature of the system remains constant." The intention, apparently, is to describe the limiting case of all theoretically possible thermostat arrangements. It will be obvious that heat cannot flow into the gas without a temperature differential between the gas and the thermostat. No matter how small this differential, an isothermal condition will not exist, but it can be

approached as a limit. The difficulty here is the same as that found in the treatment of the work done by expansion, and it can be overcome in the same way. There is no real need, however, to complicate the system by adding any kind of thermostat; it is sufficient to postulate isothermal conditions and proceed mathematically.

CONCLUSION

Perhaps the key to the real nature of the reversible process, if it be a process at all, may be found in the previous reference to Guggenheim, quoted here more fully:

All the independent infinitesimal processes that might conceivably take place may be resolved into three kinds: "natural" processes, "unnatural" processes, and "reversible" processes. "Natural" processes are all such as actually do occur in nature; examples are the interdiffusion of two gases, the equalization of pressures, and in general any approach towards complete equilibrium. An "unnatural" infinitesimal process is one that is the exact opposite of some natural process; they never occur in nature. As a limiting case between natural and unnatural processes we have "reversible" processes; they consist of a passage of a system in either direction through a continuous series of states of equilibrium.

Guggenheim has here divided all processes into two classes, those that do occur in nature and those that do not. These two classes, in the language of logic, are mutually exclusive and together exhaust the possibilities. Any third class, to which reversible processes are here said to belong, must therefore be an empty class—that is, a class with no members.

The term "reversible process" is, of course, deeply embedded in thermodynamic writing and it would be difficult, however desirable, to replace it by any other. From the foregoing it should be clear that any changes at all under the conditions of "reversibility" are not even theoretically possible, if we are to retain the fundamental concepts of mechanics. If a reversible change

be defined as that change producing the limiting value of the amount of energy convertible from one form to another and we proceed to examine the conditions necessary to yield the limiting value, we discover that such a change must take place in an equilibrium state which, by definition, is a state of no change at all. Thus the term "reversible process," unfortunately, contains a contradiction within itself, a contradiction which text book writers are prone to ignore.

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